Hybrid catalysts for the selective catalytic reduction (SCR) of NO by NH$_3$. On the role of fast SCR in the reaction network

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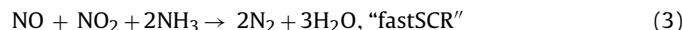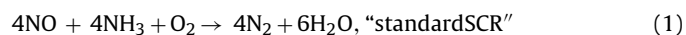*Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany*

A B S T R A C T

The SCR of NO by NH$_3$ was studied with hybrid catalysts, in which an oxidation component (Mn-Cu or Ce-Zr mixed oxides) and SCR catalysts of different activities in fast SCR (Fe-ZSM-5 of different Fe content and H-ZSM-5) are combined in physical mixtures. Fast SCR, which is SCR of NO$_2$/NO mixtures, is believed to be the final step of the reaction mechanism causing the synergy and being initiated by NO$_2$ formation over the oxidation component. In our studies, no correlation between fast-SCR activity of the SCR component and the performance of the hybrid was observed. In addition, a hybrid catalyst was found that provided rates of standard SCR significantly exceeding rates in fast SCR achieved by the SCR component alone in a wide temperature range. Therefore, fast SCR is not part of the reaction sequence causing the drastic synergetic effects between the components.

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1. Introduction

While the selective catalytic reduction (SCR) of nitrogen oxides with ammonia (ex urea) is being commercialized for NOx abatement in lean-engine driven vehicles [1], the search for stable catalysts with good low-temperature performance remains to be important and promising. Stakheev et al. [2,3] have recently demonstrated a principle which may become productive in this search. They showed that physical mixtures of catalysts active in NO oxidation and in SCR can produce strong synergetic effects in standard SCR (1), with conversions far exceeding those obtained with the individual components in a temperature range of practical relevance. This was ascribed to a mechanism according to which standard SCR proceeds as a sequence of NO oxidation (2) and fast SCR (3), which is accelerated by superior NO$_2$ formation rates over the oxidation catalyst.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O, \text{ "standardSCR''}\tag{1}$$

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2\tag{2}$$

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O, \text{ "fastSCR''}\tag{3}$$

In recent studies, our group has explored these synergies for a number of oxidation components combined with Fe-ZSM-5 [4,5] and V$_2$O$_5$-WO$_3$/TiO$_2$ [5]. In this work, it was found that the synergetic effects observed with these hybrid catalysts (or combicats) were not clearly correlated with the NO oxidation activities of the oxidation component: while good NO oxidation catalysts produced strong synergies, a comparable effect was obtained also with a material of clearly inferior NO oxidation activity (Mn-Cr mixed oxide) [4]. In [5], we reported that the performance of the hybrid catalysts strongly depends on the distance between the oxidation and SCR components. Mixing separate particles of oxidation component (e.g. Mn$_2$O$_3$, Ce-Zr or Mn-Cu mixed oxides) and SCR component (Fe-ZSM-5 or V$_2$O$_5$-WO$_3$/TiO$_2$) caused drastic deterioration of the hybrid systems, which were very effective when both components were compacted into particles together. Arranging the system in layers resulted in a complete loss of the synergy, which casts additional doubt on the view that the latter is mediated by the stable NO$_2$ molecule. In the present paper, the role of fast SCR in the reaction mechanism has been addressed by combining an oxidation component with a series of catalysts with different fast-SCR activities.

2. Experimental

In the present study, the SCR component was either Fe-ZSM-5 or H-ZSM-5. The latter was made by calcination of a commercial

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NH_4-ZSM-5 (Si/Al $\approx$ 14, Tricat Zeolites, Bitterfeld, now a Clariant company) at 773 K. Fe-ZSM-5 was introduced into the H form by solid-state ion exchange (SSIE) as described in detail by Schwidder et al. [6]. The procedure consists of grinding the zeolite with a given amount of $FeCl_3 \cdot 6H_2O$, heating the mixture at 573 K for 1 h in inert gas, washing, drying and calcination in synthetic air (20% O_2 in He) at 873 K for 2 h. Samples employed in this work contained 0.2, 0.4, and 5.1 wt-% as determined by ICP-OES. Oxidation components employed in this study were based on Ce or Mn oxides. The Mn-based component was a commercial Mn-Cu mixed oxide (hopcalite), which was donated by Carus Corporation. The ceria-zirconia mixed oxide was a commercial product donated by Umicore & Co. KG Hanau (Germany) and was used without further analysis. These components will be abbreviated as MnCu and CeZr in hybrid labels.

The hybrids were prepared by grinding oxidation and SCR component together in a mortar in a 1/1 wt ratio, pressing, crushing, and sieving to obtain an appropriate particle size for the catalytic evaluation (250–350 μm, 45–60 mesh). The labels used for the hybrids hereafter follow the structure Ox/X(y.z)-ZSM-5, with "Ox" reporting the oxidation component, y.z the Fe content of the zeolite, and X being either Fe or H.

Catalytic data of standard SCR were measured in flow regime (microflow quartz reactor, 4.2 mm i.d.) at atmospheric pressure and temperatures between 373 and 873 K. Gas lines after and before the reactors were kept at 350 K to avoid water condensation, in case of fast SCR at 420 K to suppress formation of NH_4NO_3. The GHSV was 300,000 h^{-1} for the hybrid catalysts (catalyst mass – 25 mg). For individual components it was adjusted to 600,000 h^{-1} (catalyst mass – 12.5 mg) in order to identify their possible contribution to the behavior of the hybrid systems. The feed consisted of 1000 ppm NO, 1000 ppm NH_3, 2 vol-% O_2, balanced with He. In some cases, the experiment was repeated to examine changes in the hybrid by exposure to the peak temperature of 873 K. Fast SCR was measured at 600,000 h^{-1} as well, with half of the NO in the feed replaced by NO_2. The temperature range was confined to 473–673 K.

In the steady state, NO, NO_2 and NH_3 concentrations were determined on-line using an XStream X2 Gas Analyzer (Rosemount Analytical; Emerson) which combines non-dispersive infrared and ultraviolet spectrometry for quantitative analysis. Nitrous oxide (N_2O) was determined with an ABB Advanced Optima Continuous Gas Analyzer (A02000 Series). Additionally, we analyzed N_2O and N_2 concentrations with a quadrupole mass spectrometer (Omnistar, Pfeiffer) calibrated by an internal standard. For measurements of fast SCR, a NH_3-trap inert towards the nitrogen oxides (Bühler) was inserted prior to the XStream to avoid ammonium nitrate formation in the cuvettes. Therefore, NH_3 conversion was evaluated from the mass-spectrometric data. Conversions were calculated according to:

$$X_i (\%) = \frac{c_{i,\,in} - c_{i,\,out}}{c_{i,\,in}} \times 100\%$$

(i – NO or NH_3). By-product formation will be reported by the concentrations of N_2O and NO_2 obtained.

3. Results

Most of the components used have been introduced earlier [4]. The hopcalite contained 40 wt-% Mn and 22 wt-% Cu, which results in a Mn/Cu ratio of ca. 2.3. Its BET surface area after an unknown thermal history was 242 m^2/g. Fe(0.4)-ZSM-5 had a BET surface area of 340 m^2/g. In the Fe-ZSM-5 samples, Fe oxides were not detected by XRD even at 5 wt-% Fe. MnCu proved completely amorphous, but after a treatment in 2% O_2/He at 873 K for 2 h it was converted into a $(CuMn)_3O_4$ spinel of ca. 32 nm average crystal size. This transformation occurred both in the absence and in the presence of Fe-ZSM-5, although the particle size in the mixture was somewhat smaller

(27 nm) [4]. After this procedure, no indication for solid-state ion exchange into the zeolite was found by the combination of XPS with X-ray induced Auger spectroscopy [4], which is a powerful tool for the detection of intra-zeolite Cu environments [7,8].

In Fig. 1a, NO and NH_3 conversions measured with hybrids composed of hopcalite and Fe-ZSM-5 containing different amounts of Fe% (5 wt-%, 0.2 wt-% Fe or the typical Fe impurity of technical zeolites on the order of 0.02%) are compared with those of the pure hybrid components. SCR activities of the pure zeolite components are clearly correlated with the Fe content, but those of the hybrids not at all. The conversions of MnCu/Fe(0.2)-ZSM-5 increased at the lower temperatures and the peak conversion achieved with this composite was highest. Above the peak temperature, the NO conversion of MnCu/Fe(5)-ZSM-5 decreased drastically paralleling the trend of the pure hopcalite. This decay was less pronounced at low Fe content where NO conversions remained positive in the whole temperature range. The most unexpected result is, however, the spectacular performance of the "SCR component" H-ZSM-5, which is not known as a good catalyst for either standard or fast SCR. Although not achieving the highest peak conversion, the hybrid with H-ZSM-5 performed similar to MnCu/Fe(5)-ZSM-5 at low temperatures while the decay at high temperatures was less steep even than for MnCu/Fe(0.2)-ZSM-5.

The same pattern can be seen in Fig. 1b, which reports a repetitive run right after cooling down the reactor at the end of the experiment shown in Fig. 1a. In this run, a spectacular result reported already in [4] was reproduced: except for an up-shift of the light-off-temperature T_{50} by ca. 25 K, the conversion curves of the hybrids were hardly changed, although the pure hopcalite had been completely deactivated during the first run. H-ZSM-5 is a suitable SCR component also with the deactivated hopcalite. The upshift of the conversion curve is somewhat more pronounced with it than with the Fe zeolites, but opposed to them, H-ZSM-5 achieved even larger peak NO conversion in the second run.

A similar observation can be made in Fig. 2, which summarizes data on side products. The high tendency to N_2O and NO_2 formation interferes with a technical significance of the hopcalite-based system (Fig. 2a, b). While both products formed abundantly over the pure hopcalite, the presence of the zeolite component suppressed N_2O to some extent, but increased release of NO_2. However, different from the run with pure hopcalite, NO_2 was released from the hybrids only when NH_3 conversion approached 100% (cf. Fig. 1a). In all cases, by-product formation was most pronounced at the highest Fe content. Notably, N_2O evolution over these composites was even more intense in the second run over the Fe-containing samples although the pure degraded hopcalite did not form any N_2O up to 630 K (Fig. 2c). Opposed to this, NO_2 formation was attenuated in the second run. Over the pure degraded hopcalite, it did not rise above the level of experimental noise up to 523 K (Fig. 2d), while synergy in the hybrids was obvious already below this temperature (Fig. 1b).

An analogous experiment with composites made from Ce-Zr and FeZSM-5 is summarized in Fig. 3. As reported in [4], composites with Ce-Zr mixed oxide are less active. Although their light-off temperatures exceed those of the hopcalite-based hybrids by ca. 150 K, a strong synergistic effect is still obvious (Fig. 3a). Again, there is no relation between Fe content in ZSM-5 and performance of the hybrids made with the zeolites: here, the composites were nearly indistinguishable except for the highest temperatures where the one with Fe(0.2)-ZSM-5 kept higher conversions. This series was now extended to the parent H-ZSM-5 as well, and the results are shown in Fig. 3b. Although slightly less active, the composite with the parent H-ZSM-5 achieved conversions of the same order of magnitude as CeZr/Fe(0.4)-ZSM-5. For the Fe-free sample, first-order rate constants calculated from the NO conversions up to 573 K are about half those obtained with the latter compos-
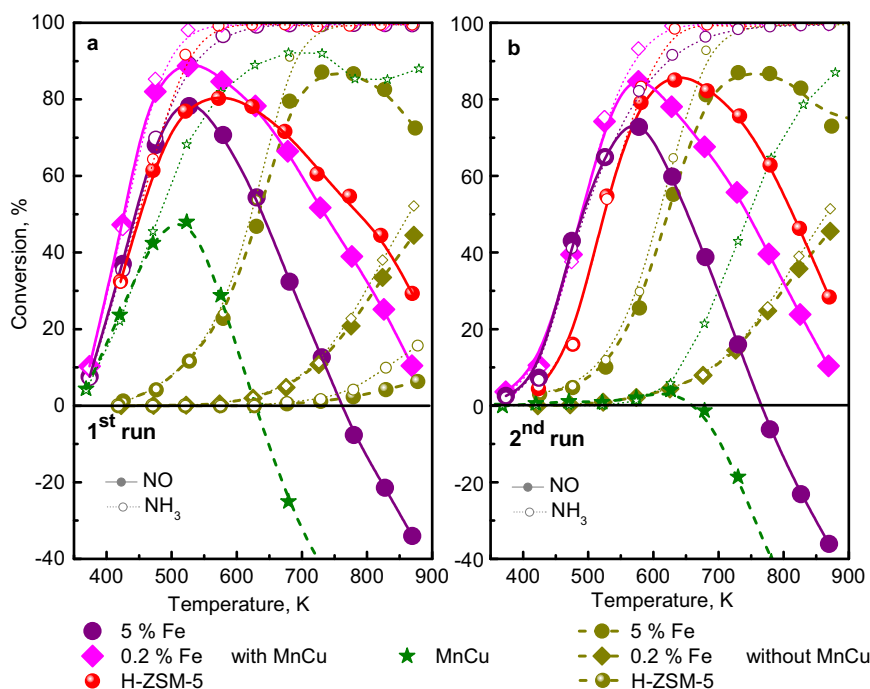
Fig. 1. NO and NH$_3$ conversions in standard SCR over MnCu/Fe-ZSM-5 mixtures and over individual mixture components MnCu (hopcalite) and Fe-ZSM-5 (0.2 or 5 wt-% Fe); (a) first run, (b) second run immediately after (a); 1000 ppm NO, 1000 ppm NH$_3$, 2% O$_2$ in He, at 300,000 h^{-1} (mixtures) or 600,000 h^{-1} (individual components).
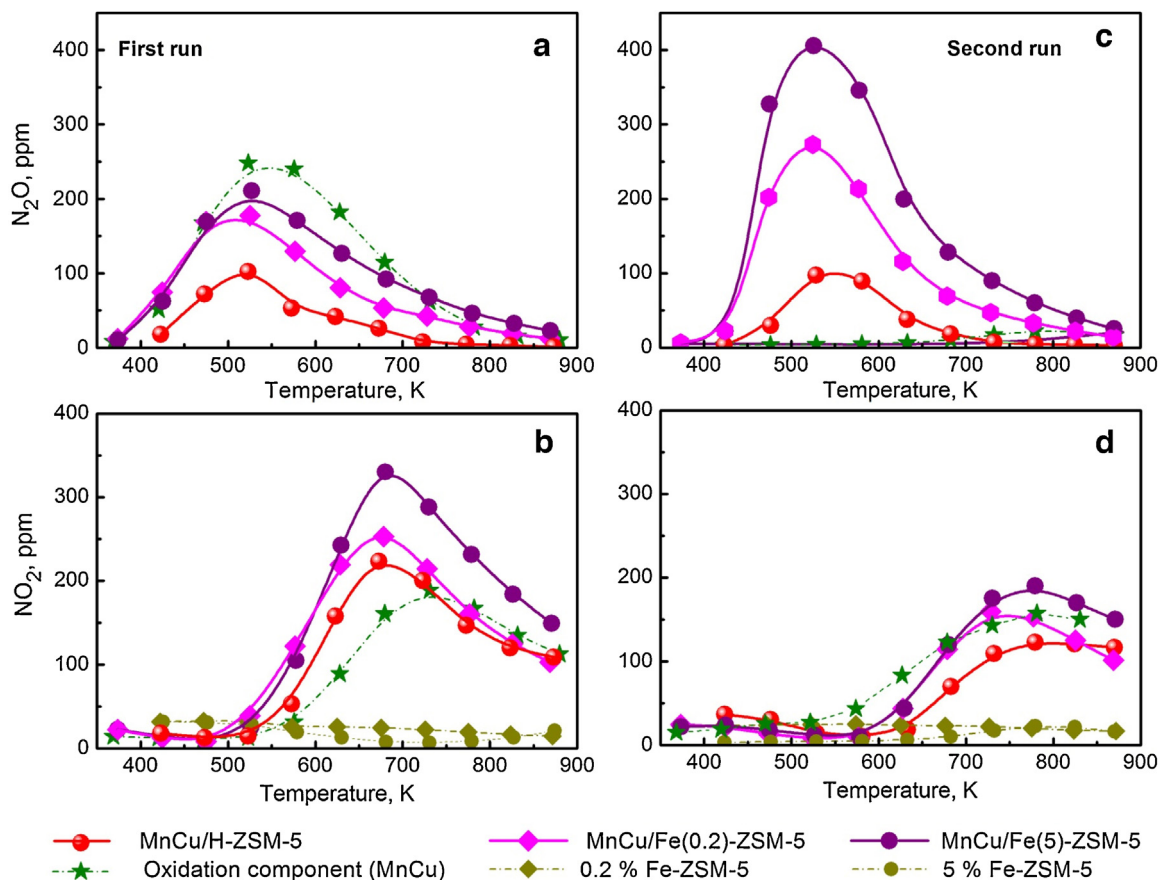
Fig. 2. By-product formation in standard SCR over MnCu/Fe-ZSM-5 mixtures and over individual mixture components MnCu (hopcalite) and Fe-ZSM-5 (0.2 or 5 wt-% Fe); (a) first run, (b) second run immediately after (a); for conditions see Fig. 1.
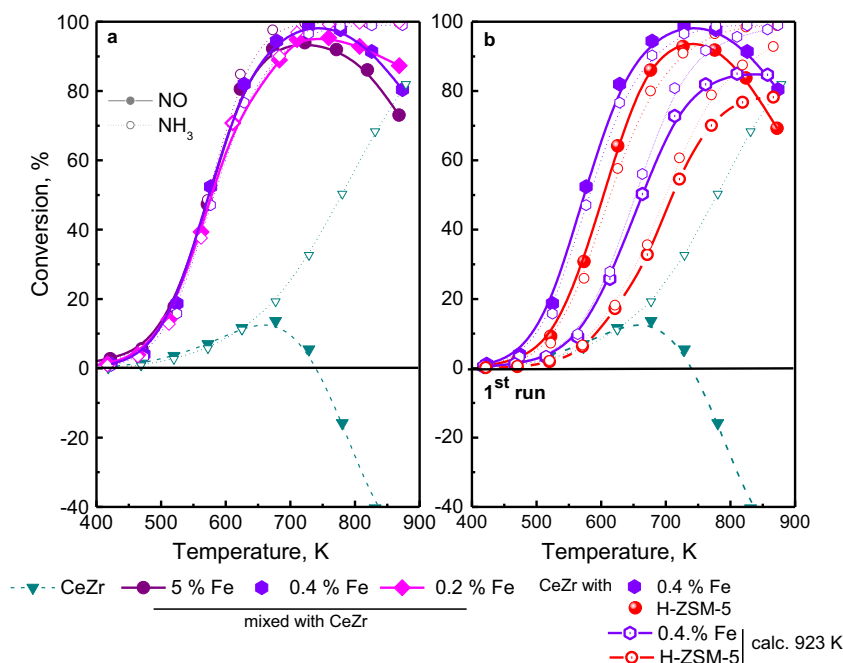
Fig. 3. NO and NH$_3$ conversions in standard SCR over Ce-Zr/X-ZSM-5 mixtures and over individual CeZrOx mixed oxide (for conversion over zeolite components – see Fig. 1a); (a) comparison of mixtures containing Fe-ZSM-5, (b) comparison of mixture of Ce-Zr with Fe(0.4)-ZSM-5 and H-ZSM-5 in fresh state and after 3 h calcination at 923 K in synthetic air. For conditions see Fig. 1.

ite. At high temperatures, the NO conversions over both hybrids decreased significantly. Surprisingly, in this respect the Fe-free sample resembled the samples with higher Fe content rather than CeZr/Fe(0.2)-ZSM-5 (cf. Fig. 3a).

By-product formation was negligible over these composites and is therefore not reported in a separate figure. In [4], a CeZr/Fe(0.4)-ZSM-5 hybrid was shown to release no detectable amounts of N$_2$O and NO$_2$ in the whole temperature range studied. This holds also for composites with different Fe contents including H-ZSM-5. Pure CeZr forms some NO$_2$ at higher temperatures, but this is completely suppressed in presence of the zeolite components.

Fig. 3b also contains curves registered after the physical mixtures of CeZr with H-ZSM-5 or Fe-ZSM-5 had been calcined at 923 K in 20% O$_2$/He for 3 h. The activity of both mixtures was strongly affected, with an up-shift of the light-off temperatures by 90 K or 110 K (CeZr with Fe(0.4)-ZSM-5 or H-ZSM-5, respectively). The ranking between the catalysts remained the same, but the hybrid with H-ZSM-5 was more deactivated than that with Fe-ZSM-5.

The behavior of the SCR components employed in the present study in the catalysis of fast SCR is summarized in Fig. 4, where panel a shows the temperature dependences of the conversion of the sum of NO and NO$_2$, panel b those of all reactants, NO, NO$_2$, and NH$_3$. As in standard SCR (cf. Fig. 1), the activities in fast SCR are ranked according to the Fe content. The curve of H-ZSM-5 has been taken from ref. [9]. Additional exchange of some Fe to reach just 0.2 wt-% boosts the activity strongly: on the basis of a first order kinetics, which is of course only a very coarse estimate, the conversions over Fe(0.2)-ZSM-5 and H-ZSM-5 at 473 K would result in a ratio of ≈20 between rate constants.

At the first sight, these observations contradict the behavior of the hybrids (Figs. 1 and 3) where the low-temperature performance depends much less on the Fe content than in fast SCR (Fig. 4). It should be noted, however, that over the Fe zeolites, the NOx conversions shown in Fig. 4 are mostly larger than the NO conversions over the hybrids at the same temperature. This would allow for an explanation according to which the oxidation step is rate limiting so that the differences in fast SCR activity of the zeolite component are not

reflected in the results. The MnCu/H-ZSM-5 composite, however, contradicts this explanation completely: it achieved a conversion of ca. 75% at 500 K (Fig. 1a) where the zeolite itself converted just above 10% of the NOx in fast SCR, though at a slightly larger GHSV (see legend). This will provide the chance to directly reject fast SCR as a step in the reaction mechanism operating in the hybrid.

4. Discussion

By studying the effect of spatial separation between the hybrid components, our group has recently shown that the synergistic effect obtained in these mixtures is not mediated by a stable component as would be NO$_2$ [5]. Instead, unstable intermediates seem to leave the surface of one component and find active sites on the other one, which convert them to the final product. This motive is reminiscent of a reaction mechanism for standard SCR recently derived by E. Tronconi's group from trapping experiments, in which nitrite adsorbates formed in the interaction of NO + O$_2$ with Fe-ZSM-5 were trapped by admixed BaO/Al$_2$O$_3$ [10,11]. Irrespective of the interpretation of the results, both Tronconi and our studies show that during SCR reactions unstable intermediates travel through the gas phase and can contribute to the reaction events measured in the experiment.

The present study was devoted to examine the feasability of fast SCR (Eq. (3)) as a step of the reaction network. If it was the slow step, the rates over the hybrids should scale with the fast-SCR activity of the SCR component, if it was a fast step, the SCR component should not affect the total standard SCR rate over the composites at all.

The latter picture is what can be observed with the Ce-Zr/X-ZSM-5 composites: there is no dependence of rates on the Fe content (Fig. 3a). The somewhat deteriorated performance of the composite of CeZr with H-ZSM-5 (Fig. 3b) might originate from the much lower fast-SCR activity of the latter: if both rates are on the same order of magnitude, the rate determining role of the oxidation step gets lost. However, the retained ranking after the high-temperature treatment (Fig. 3b) is in conflict with this explanation. As dry calcination at 923 K should not damage the zeolites
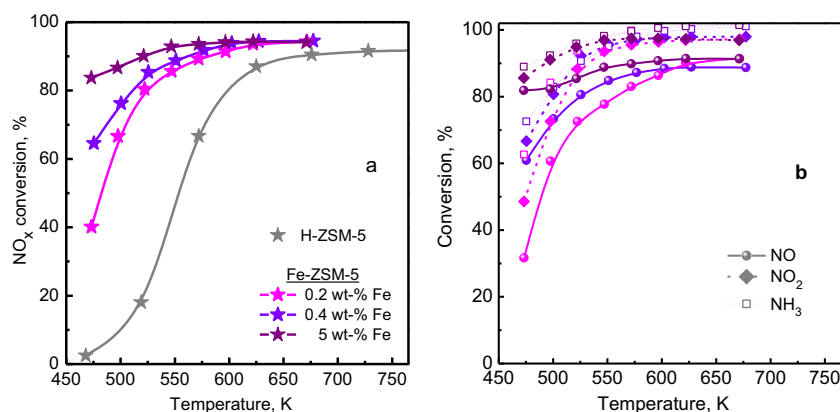
Fig. 4. Fast SCR over SCR components employed in this study, (a) average of NO and NO$_2$ conversions, (b) conversions of individual components NO, NO$_2$, and NH$_3$; 500 ppm NO, 500 ppm NH$_3$, 2% O$_2$ in He, at 600,000 h^{-1} (for H-ZSM-5 – 750,000 h^{-1}).

(the Fe-ZSM-5 had even been calcined at this temperature before), the loss in activity should result from a deactivation of the oxidation component. This deactivation would cause a difference in the rates of oxidation and SCR steps, making the former rate determining. As the oxidation component is the same in both composites, their performance should converge after calcination. In fact, the opposite was observed.

With the Mn-Cu-based composites conclusions regarding the role of fast SCR are more straightforward. Activities obtained with Fe-ZSM-5 of very diverse Fe contents differ significantly (Fig. 1a), which should not be the case if the oxidation step was rate limiting. If we were in the vicinity of the transition region, the zeolite with the smaller fast-SCR activity should produce the less active composite. In reality, the opposite occurs, and even H-ZSM-5, which cannot compete with the Fe zeolites with respect to its fast-SCR performance, works well with the hopcalite. Indeed, standard SCR rates over MnCu/H-ZSM-5 exceeded those for fast SCR over the zeolite component alone in a wide temperature range (cf. Figs. 1 a, 4 a). In literature, there are examples for H-zeolites exhibiting significantly higher activity in fast SCR than our sample [12,13]. However, by comparing the behavior of the latter with that of a H-ZSM-5 void of any Fe impurity, we have shown recently that fast SCR rates provided by acidic sites are much lower than those caused by the Fe impurity [9]. According to results presented in the same paper, fast SCR activity results from a very small number of highly active sites (cf. also [14]). Indeed, deliberate exchange of just 0.2 wt-% Fe into the zeolite increases the activity by a further order of magnitude (Fig. 4). The activity of a H zeolite for fast SCR is therefore most likely dominated not just by the concentration of the Fe impurity, but also by its speciation, which may explain the wide spread in activities observed with different samples. Comparing rates of fast SCR over a rather inactive H-ZSM-5 and of standard SCR over a MnCu/H-ZSM-5 made with the same zeolite indeed excludes fast SCR as a part of the reaction network of standard SCR in these hybrid catalysts.

The striking differences between the composites with respect to side product formation raise a number of problems which cannot be solved at present. Fig. 2c shows a drastic N$_2$O formation of a composite, the components of which do not form any N$_2$O when reacting alone (for the degraded hopcalite this is shown by the run reported just in Fig. 2c). At the same time, the degraded hopcalite does not convert NO and NH$_3$ at all to a significant extent up to 573 K (Fig. 1c). This means that there must be almost complete reversibility in the formation of the intermediate: If it does not find suitable sites for ongoing chemistry, it decomposes into the original reactants.

The differences in the results of "ongoing chemistry" obtained in our systems are most surprising because the zeolites offered

for these processes are the same in both systems studied. On the Ce-Zr-based hybrids, there is no N$_2$O formation whatsoever while the hybrids with degraded hopcalite (Fig. 2c) form this product abundantly. This contrast is difficult to understand on the basis of a source emitting just one labile intermediate species into the zeolite component: the role of the oxidation component seems to go beyond the production of this single intermediate species. Hypotheses to be examined in further work on these systems include the case that different species are emitted by different oxidation components, and the case that the reaction cascade may return from the zeolite to the surface of the oxidation component. In the latter case, the reaction space would be confined to the voids between the crystals of zeolite and oxidation component, maybe including the outermost layers of the zeolite crystal. Potential intermediates that have been discussed in recent literature are HNO$_2$ [10,11] and NH$_2$NO, which has been postulated in theoretical studies [15,16]. However, given the strong dependence of the synergistic effect on the distance between the components [5], radical species as discussed e.g. in [15] should not be ruled out.

5. Conclusions

In hybrid catalysts for standard SCR that consist of an oxidation component combined with SCR catalysts of different activities in fast SCR, no correlation between fast-SCR activity of the latter and the performance of the hybrid was observed. While this might indiciate a rate-limiting role of the oxidation step assumedly combined with fast SCR, any role of the latter in the catalytic mechanism was rejected by the development of a hybrid catalyst which exhibited significantly larger standard SCR rates compared to fast SCR rates over the SCR component alone in a wide temperature range. Therefore, fast SCR is not part of the reaction sequence causing the drastic synergistic effects between the components in the catalysis of standard SCR.

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